

# Spin-polarization-induced structural selectivity in $\text{Pd}_3X$ and $\text{Pt}_3X$ ( $X = 3d$ ) compounds

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Spin-polarization is known to lead to important *magnetic* and *optical* effects in open-shell atoms and elemental solids, but has rarely been implicated in controlling *structural* selectivity in compounds and alloys. Here we show that spin-polarized electronic structure calculations are crucial for predicting the correct  $T = 0$  crystal structures for  $\text{Pd}_3X$  and  $\text{Pt}_3X$  compounds. Spin-polarization leads to (i) stabilization of the  $L1_2$  structure over the  $DO_{22}$  structure in  $\text{Pt}_3\text{Cr}$ ,  $\text{Pd}_3\text{Cr}$ , and  $\text{Pd}_3\text{Mn}$ , (ii) to the stabilization of the  $DO_{22}$  structure over the  $L1_2$  structure in  $\text{Pd}_3\text{Co}$  and to (iii) ordering (rather than phase-separation) in  $\text{Pt}_3\text{Co}$  and  $\text{Pd}_3\text{Cr}$ . The results are analyzed in terms of first-principles local spin density calculations.

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Crystal structure compilations [1,2] reveal that the most commonly occurring structures among intermetallic binary compounds with a 3:1 stoichiometry ( $A_3B$ ) are the cubic  $L1_2$  and the tetragonal  $DO_{22}$  (Fig. 1). The crystallographic difference between the  $L1_2$  and  $DO_{22}$  structures is rather subtle: the two structures have identical *first* neighbor coordination (each  $A$  has  $8A + 4B$  neighbors and each  $B$  has  $12A$  neighbors) while a difference exists in the *second* shell (see Fig. 1). The manner in which particular  $A_3B$  compounds select the  $L1_2$  or the  $DO_{22}$  configuration appears to be rather interesting. For example, [2] the 4d trialuminides  $\text{Al}_3M$  show the sequence  $L1_2 \rightarrow L1_2 \rightarrow DO_{22}$  as  $M$  varies across the 4d row  $\text{Y} \rightarrow \text{Zr} \rightarrow \text{Nb}$ , while the 3d palladium alloys  $\text{Pd}_3X$  show  $L1_2 \rightarrow L1_2 \rightarrow DO_{22} \rightarrow L1_2 \rightarrow L1_2 \rightarrow L1_2$  as one proceeds in the 3d row  $X = \text{Sc} \rightarrow \text{Ti} \rightarrow \text{V} \rightarrow \text{Cr} \rightarrow \text{Mn} \rightarrow \text{Fe}$  [3] (for  $X = \text{Co}$  and  $\text{Ni}$ , the systems phase-separate). The origin of such regularities was the subject of numerous investigations including the  $d$ -electron “generalized perturbation method” (GPM), [4] and first-principles calculations. [5–7] However, these calculations failed to reproduce the observed structural trends. These calculations were non-magnetic (NM, i.e., without spin-polarization). This appeared to be a reasonable assumption, since one expects that an alloy rich in a non-magnetic component (e.g.,  $\text{Pd}_3\text{Cr}$ ) or one without any magnetic components (e.g.,  $\text{Pd}_3\text{V}$ ) will not have any significant magnetic effects. We demonstrate here that spin-polarization have a crucial influence on the structural stability of  $\text{Pd}_3X$  and  $\text{Pt}_3X$  compounds: it stabilizes the observed  $L1_2$  structure over the  $DO_{22}$  structure in  $\text{Pt}_3\text{Cr}$ ,  $\text{Pd}_3\text{Cr}$ , and  $\text{Pd}_3\text{Mn}$ , the  $DO_{22}$  structure over the  $L1_2$  structure in  $\text{Pd}_3\text{Co}$ , and is responsible for compound formation (rather than phase-separation) in  $\text{Pt}_3\text{Co}$  and  $\text{Pd}_3\text{Cr}$ .

The key insight to stability in compounds and alloys has traditionally been the association of stability with low density of states (DOS) at Fermi energy  $E_F$ . [8]

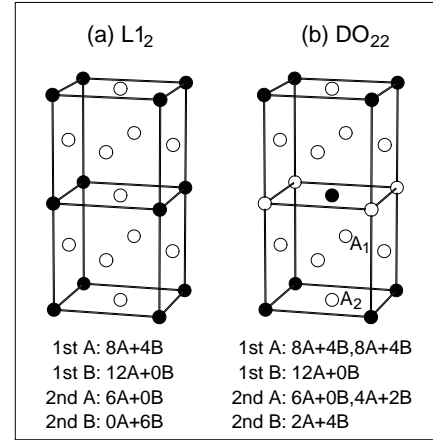


FIG. 1. The crystal structures of the (a)  $L1_2$  and (b)  $DO_{22}$  structures. The insert shows the atomic coordination about  $A$  and  $B$  sites in the first (1st) and second (2nd) atomic shells.  $A_1$  and  $A_2$  indicate two distinct  $A$  sites in the  $DO_{22}$  structure.

Nicholson *et al.* [5] noted that for transition metal aluminides the more stable of the two structures ( $L1_2$  or  $DO_{22}$ ) corresponds to the one with smaller DOS at the Fermi-level,  $N(E_F)$ . Local density approximation (LDA) [9] band structure and total energy calculations [6,7] have later substantiated this relation. To examine such a relation for inter-transition metal  $A_3B$  compounds rather than aluminides we have calculated  $N(E)$  (Fig. 2) and total energy difference  $\delta E = E(L1_2) - E(DO_{22})$  [Fig. 3(a) and Table I] for  $\text{Pd}_3X$  with 3d atom  $X = \text{Sc}$  through  $\text{Cu}$  using the NM linearized augmented plane wave (LAPW) method. [11] We see that the structure with the lower calculated NM total energy (Table I) indeed has a lower calculated NM  $N(E_F)$  (Fig. 2), thus substantiating earlier trends for aluminides. [5–7] For example, for  $\text{Pd}_3X$  with  $X = \text{V}$ ,  $\text{Cr}$ , and  $\text{Mn}$ , the Fermi energy,  $E_F$ , falls near a DOS *maximum* for  $L1_2$  but near a DOS *mini-*

*mum* for  $DO_{22}$ ; correspondingly  $E(DO_{22})$  is lower than  $E(L1_2)$ . Unfortunately, while the magnitude of  $N(E_F)$  is indicative of the stability of the *calculated* structure, these non-magnetic calculations incorrectly predict the *observed* stable crystal structure in several cases: while  $Pd_3V$  is correctly predicted to be more stable in the  $DO_{22}$  structure, the *observed* [2] stable structure for  $Pd_3Cr$ ,  $Pd_3Mn$ , [3] and  $Pd_3Fe$  is the  $L1_2$  structure, not the non-magnetically predicted  $DO_{22}$  structure. Thus, while the correlation between the *calculated* quantities  $N(E_F)$  versus  $E(L1_2) - E(DO_{22})$  holds, it leads to incorrect predictions for the stability of  $Pd_3Cr$ ,  $Pd_3Mn$ , and  $Pd_3Fe$ . The generalized perturbation method calculations, [4] based on similar DOS arguments [diamond symbols in Fig. 3(a)] likewise predicts  $Pd_3Cr$ ,  $Pd_3Mn$ , and  $Pd_3Fe$  (and even  $Pd_3Sc$  and  $Pd_3Ti$ ) to be stable in the  $DO_{22}$  structures, in conflict with experiment. [2] In this paper we explain this puzzle by noting that while a large  $N(E_F)$  indeed implies a *destabilizing* factor for the one-electron (“band”) energy, it also leads (in open-shell systems) to spin-polarization and magnetic moment formation which, in turn, is a *stabilizing* factor. Thus, despite their large  $N(E_F)$  in the  $L1_2$  structure (suggesting one-electron *instability*),  $Pt_3Cr$ ,  $Pd_3Cr$  and  $Pd_3Mn$  (nearly so for  $Pd_3Fe$ ) are correctly predicted to be more stable in this structure once *spin-polarized* total energy calculations [10] are done. Thus, magnetic ordering changes the predictions of NM total energy calculations and restores agreement with experiment.

We have calculated the total energies of  $Pd_3X$ , for  $X = Sc$  through  $Cu$  as well as  $Pt_3Cr$  and  $Pt_3Co$  in the  $L1_2$  and  $DO_{22}$  structures using the LDA in both the spin-polarized and spin-unpolarized versions [12] of the full-potential LAPW method. [11] In order to accurately

TABLE I. LDA calculated total energy difference (in meV/atom)  $\delta E = E(L1_2) - E(DO_{22})$  and the ferromagnetic (FM) DOS at Fermi energy  $N(E_F)$  (in states/eV spin) for the  $L1_2$  and  $DO_{22}$  structures. Note that the spin-polarization (included in the FM state) reverses the relative stability of non-magnetic (NM)  $L1_2$  and  $DO_{22}$  structures for those compounds marked by an asterisk, thus restoring agreement with experiment. [2,3]). PS denote phase-separation.

	Expt Structure	$\delta E_{NM}$	$\delta E_{FM}$ $L1_2$	$N_{FM}(E_F)$ $DO_{22}$	$N_{FM}(E_F)$
$Pd_3Sc$	$L1_2$	-102	-102	0.34	0.65
$Pd_3Ti$	$L1_2$	-48	-48	0.14	0.28
$Pd_3V$	$DO_{22}$	71	40	0.64	0.38
$Pd_3Cr$ *	$L1_2$	74	-20	0.57	0.60
$Pd_3Mn$ *	$L1_2$	48	-45	0.59	0.80
$Pd_3Fe$	$L1_2$	14	1	0.42	0.34
$Pd_3Co$ *	PS	-5	15	0.79	0.46
$Pd_3Ni$	PS	-2	0	0.95	0.93
$Pd_3Cu$	$L1_2$	-8	-8	0.52	0.92
$Pt_3Cr$ *	$L1_2$	71	-23	0.56	0.54
$Pt_3Co$	$L1_2$	-11	-16	0.66	0.65

obtain the small energy difference between two fairly similar crystal structures, the calculations were carried out consistently using the same muffin-tin radii,  $R_{MT}$ , and basis set energy cutoffs,  $K_{max}$ . The Brillouin Zone summations were done using the geometrically equivalent  $\mathbf{k}$ -point sampling scheme” [13](a), in which 20 (40)  $\mathbf{k}$ -points in the irreducible zone for the  $L1_2$  ( $DO_{22}$ ) structure is mapped into the same 60 special  $\mathbf{k}$ -points [13](b) in the fcc structure. We optimized the total energy as a function of volume, as well as the  $c/a$  ratio in the  $DO_{22}$  structure. The estimated LAPW error for the  $E(L1_2) - E(DO_{22})$  energy difference is  $\sim 5$  meV/atom, and the neglected zero-point energy difference between the two similar structures should be even smaller. At zero temperature, the *absolute stability of a compound in a structure  $\sigma$*  with respect to phase separation is given by its formation enthalpy  $\Delta H(\sigma)$

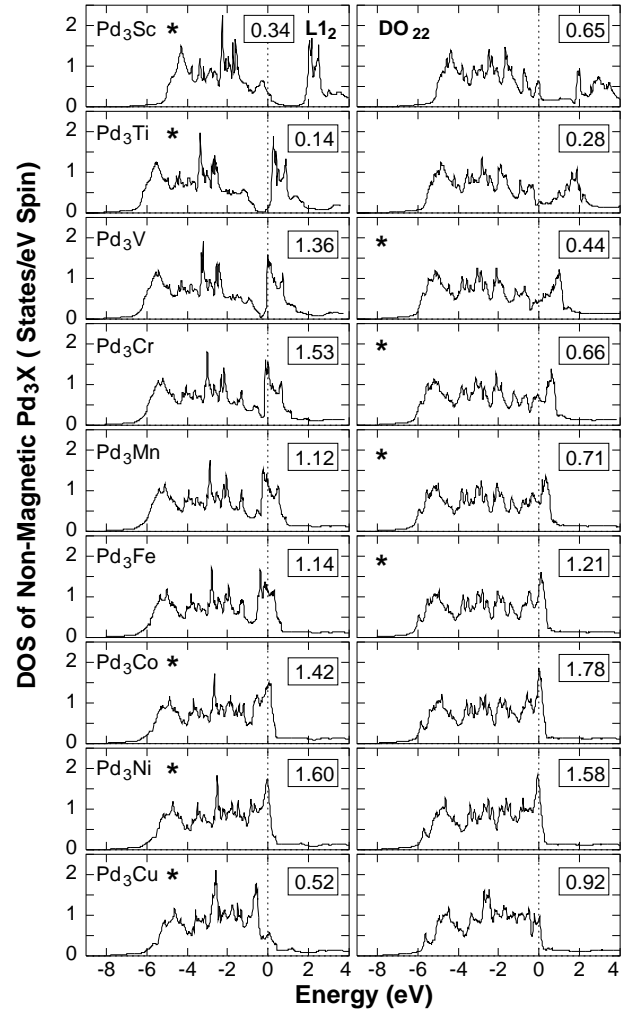


FIG. 2. LDA calculated NM total DOS for  $Pd_3X$  in the  $L1_2$  and  $DO_{22}$  structures. The inserts denote  $N(E_F)$ . An asterisk denotes the more stable structure predicted by total energy calculations in the absence of magnetic ordering. Note that the more stable structure has a lower  $N(E_F)$ .

$$\Delta H_\alpha(\sigma) = E_\alpha(\sigma) - x_A E_A(V_A) - x_B E_B(V_B) \quad (1)$$

where  $E_A(V_A)$  and  $E_B(V_B)$  are the energies of the constituents  $A$  and  $B$  in their respective ground states (e.g., for  $\text{Pd}_3\text{Ni}$ , it is non-magnetic fcc for Pd and ferromagnetic fcc for Ni),  $E_\alpha(\sigma)$  is the energy of structure  $\sigma$ ,  $\alpha = \text{NM}$  or  $\text{FM}$  denotes whether structure  $\sigma$  is in the non-magnetic or ferromagnetic states. The *relative stability of two different ordered structures* is,

$$\delta E_\alpha = E_\alpha(L_{12}) - E_\alpha(DO_{22}) \quad (2)$$

while the *magnetic stabilization energy of a given structure  $\sigma$  ( $L_{12}$  or  $DO_{22}$ )* is

$$\delta M(\sigma) = E_{\text{FM}}(\sigma) - E_{\text{NM}}(\sigma) \quad (3)$$

Table I and Fig. 3(a) give  $\delta E_{\text{NM}}$  and  $\delta E_{\text{FM}}$ , while Fig. 3(b) shows the magnetic stabilization energies  $\delta M(L_{12})$  and  $\delta M(DO_{22})$ , and the local magnetic moment  $\mu_X$  on the  $X$  atom calculated numerically within the muffin-tin sphere (the value of  $\mu_X$  is rather insensitive to the small change in muffin-tin radius).

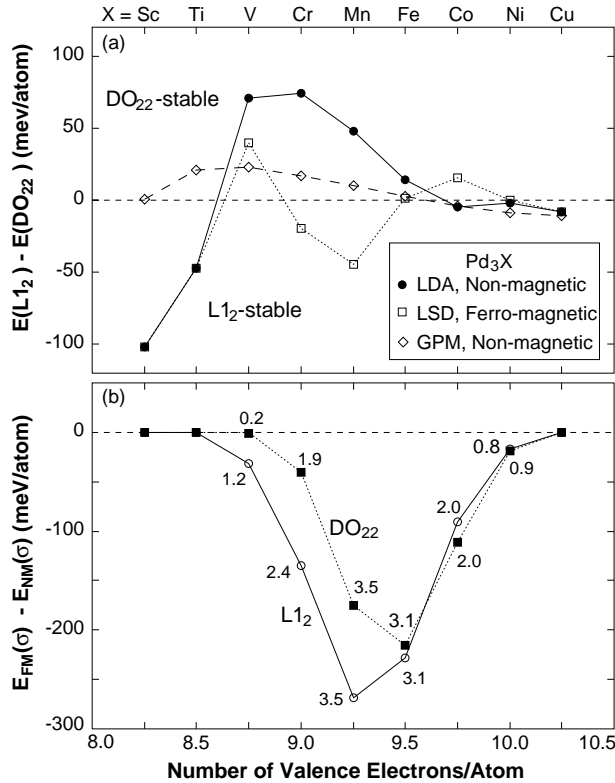


FIG. 3. (a) LDA (present) and GPM (Ref. [4]) calculated energy difference  $\delta E = E(L_{12}) - E(DO_{22})$  [Eq. (2)] for  $\text{Pd}_3X$  compounds. Note the reversal of sign for  $\delta E$  due to spin-polarization for  $\text{Pd}_3\text{Cr}$ ,  $\text{Pd}_3\text{Mn}$ , and  $\text{Pd}_3\text{Co}$  (nearly so for  $\text{Pd}_3\text{Fe}$ ). Part (b) gives the magnetization energies  $\delta M(\sigma) = E_{\text{FM}}(\sigma) - E_{\text{NM}}(\sigma)$  [Eq. (3)] for  $\sigma = L_{12}$  (empty circles) and  $\sigma = DO_{22}$  (solid squares) structures and shows the local magnetic moment for the  $X$  atom (numbers above or below the symbols).

Table II gives the formation enthalpies  $\Delta H_\alpha(L_{12})$  and  $\Delta H_\alpha(DO_{22})$  for several systems. Figure 2 depicts the NM total DOS for  $\text{Pd}_3X$ , where  $X = \text{Sc} \rightarrow \text{Cu}$ , in the  $L_{12}$  (left panel) and  $DO_{22}$  structures (right panel). One notices the following:

(i) In contrast to the very similar DOS for the  $L_{12}$  and  $DO_{22}$  structures and the small energy difference  $E(L_{12}) - E(DO_{22}) \sim 20$  meV/atom predicted by the GPM, [4] one sees from Fig. 2 a marked difference of the DOS in the  $L_{12}$  and  $DO_{22}$  structures. (a) While the DOS of the cubic  $L_{12}$  structure resemble that of fcc Pd, having three major peaks, the DOS of the  $DO_{22}$  structure are more smeared, reflecting a loss of cubic symmetry in the  $DO_{22}$  structure. (b) The DOS of the more stable  $L_{12}$  structure for  $\text{Pd}_3\text{Sc}$  and  $\text{Pd}_3\text{Ti}$  shows a “pseudo-gap” near the Fermi level absent in the  $DO_{22}$  structure. (c) In the  $L_{12}$  structure, the Fermi level of  $\text{Pd}_3\text{V}$ ,  $\text{Pd}_3\text{Cr}$ , and  $\text{Pd}_3\text{Mn}$  falls on a DOS peak (made mostly of  $d$  orbitals of the  $X$  atom), while in the  $DO_{22}$  structure the Fermi level falls on a relatively flat portion of the DOS. Indeed, these materials are more stable in the  $DO_{22}$  structure in a NM LDA description. As a result of these differences, the values of the  $N(E_F)$  (given in the inserts of Fig. 2) and its shape near the Fermi level are strikingly different for the  $L_{12}$  and  $DO_{22}$  structures.

(ii) The above noted trends in the NM  $N(E_F)$  induce a concomitant magnetic stabilization energy  $\delta M$  [Fig. 3(b)]: A *larger* energy stabilization  $\delta M$  due to spin-polarization relates with a *larger*  $N(E_F)$  and with a *larger* localized magnetic moment  $\mu_X$  on the  $X$  atom [Fig. 3(b)]. For example, while the  $\text{Pd}_3X$  compounds with  $X = \text{Sc}$ ,  $\text{Ti}$ , and  $\text{Cu}$  are non-magnetic (so  $\delta M = 0$ ), when  $X = \text{Mn}$  and  $\text{Fe}$ , one sees in Fig 3(b) large energy lowering due to spin-polarization ( $\delta M \sim -200$  meV/atom), and concomitantly large magnetic moments of  $3.5 \mu_B$  ( $X = \text{Mn}$ ) and  $3.1 \mu_B$  ( $X = \text{Fe}$ ) in both the  $L_{12}$  and  $DO_{22}$  structures (as a comparison, bcc Fe has a magnetic moment value of only  $2.2 \mu_B$ ). Thus, spin-polarization induces a local magnetic moment on the “magnetic”  $3d$ -atoms with large NM  $N(E_F)$  while lowering the total energy of the compound. In the case of  $\text{Pt}_3\text{Cr}$  in the  $L_{12}$  structure for which previous calculation exists, our calculated total magnetic moment in the unit cell ( $2.6 \mu_B$ ) agrees with a

TABLE II. Non-magnetic (NM) and Ferromagnetic (FM) formation enthalpies,  $\Delta H$  [in meV/atom, Eq. (1)], of some compounds.  $\Delta H$ 's are taken with respect to the NM fcc Pd, Pt, FM fcc Ni, FM fcc Co, and anti-FM bcc Cr, respectively.

	$\Delta H(L_{12})$		$\Delta H(DO_{22})$	
	NM	FM	NM	FM
$\text{Pd}_3\text{Cr}$	126	-9	51	11
$\text{Pd}_3\text{Co}$	155	64	160	49
$\text{Pd}_3\text{Ni}$	61	43	62	44
$\text{Pt}_3\text{Cr}$	-68	-185	-139	-161
$\text{Pt}_3\text{Co}$	31	-42	42	-26

previous calculation [14] of  $2.6 \mu_B$  and with the experimental value [15] of  $2.5 \mu_B$ .

(iii) In the NM calculations,  $\text{Pd}_3\text{V}$  and  $\text{Pd}_3\text{Cr}$  have large DOS peaks at  $E_F$  in the  $L1_2$  structure, and are concomitantly less stable in this structure than in the low  $N(E_F)$   $DO_{22}$  structure. However, as spin-polarization is introduced, the large DOS peak of the  $L1_2$  structure splits, so that  $E_F$  now resides in a low DOS region. This leads, simultaneously, to the formation of larger magnetic moments on V and Cr in the  $L1_2$  structure relative to the  $DO_{22}$  structure. This selective magnetization thus lowers the energy of the  $L1_2$  structure more significantly than in the  $DO_{22}$  structure [Fig. 3(b)].

(iv) Table I shows that the more stable of the two structures generally (and weakly) relates with a smaller value of the *ferromagnetic* DOS at the Fermi level  $N_{\text{FM}}(E_F)$ . Thus, the trend of total energy stability with  $N(E_F)$  does exist, but for the spin-polarized quantities.

(v) The magnetic stabilization energy  $\delta M$ , reverses the relative stability predicted by NM calculations in several cases: spin-polarization stabilizes the experimentally observed [2]  $L1_2$  structure of  $\text{Pd}_3\text{Cr}$ ,  $\text{Pd}_3\text{Mn}$ , and  $\text{Pt}_3\text{Cr}$  (nearly so for  $\text{Pd}_3\text{Fe}$ ) over the  $DO_{22}$  structure, while for  $\text{Pd}_3\text{Co}$ , spin-polarization makes the  $DO_{22}$  structure more stable. The reversal of stability for  $\text{Pd}_3\text{Co}$  can not be observed experimentally, since the calculated  $\Delta H$  [Eq. (1) and Table II] is *positive*, so  $\text{Pd}_3\text{Co}$  (and similarly,  $\text{Pd}_3\text{Ni}$ ) is predicted to phase separate rather than to order, in accord with the observed phase-separation behaviors for Pd-Co and Pd-Ni. [2]

(vi) Spin-polarization can stabilize ordering over phase-separation: [16] We find that in a NM description  $\text{Pt}_3\text{Co}$  has  $\Delta H_{\text{NM}} > 0$  so it is predicted to phase separate, but that a strong spin-polarization effect stabilizes the ordered  $L1_2$  structure, leading to  $\Delta H_{\text{FM}} < 0$  in agreement with the observed ordering behavior. [2] Similarly, spin-polarization stabilizes the experimentally observed [17]  $L1_2$  structure of  $\text{Pd}_3\text{Cr}$  (its magnetic behavior has, however, not been experimentally examined). Hence, spin-polarization not only reverses the stability of the  $L1_2$  and  $DO_{22}$  structures for many compounds, but it also stabilizes an ordered ( $L1_2$ ) structure over phase-separation for  $\text{Pd}_3\text{Cr}$  and  $\text{Pt}_3\text{Co}$ .

(vii) Interestingly, the  $\Delta H$  for  $\text{Pt}_3\text{Cr}$  are negative in both the NM and FM cases, but the spin-polarization effect gives a larger stability to the  $L1_2$  structure (observed experimentally). [2] One also notices that the  $\Delta H$  are lower in the Pt alloys than in the corresponding Pd alloys. The increased stability in Pt alloys has been addressed previously in Ref. [16].

In summary, we have shown that a theoretically unstable non-magnetic structures which involve magnetic atoms and possesses *large*  $N(E_F)$ , may be stabilized by splitting the near  $E_F$  peak in the DOS and forming a local magnetic moment with a concomitant *lowering* of  $N(E_F)$  and the total energy. Therefore, theoretical stud-

ies of the stability of compounds with a large value of a NM  $N(E_F)$  should be carefully tested for magnetic ordering which can often change the predictions of the ground state crystal structure.

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